

N 94-16814

## NITROGEN ISOTOPIC SIGNATURES IN AGGLUTINATES FROM BRECCIA 79035

John F. Kerridge, Yoosook Kim, Jin S. Kim &amp; Kurt Marti, Dept. Chemistry, UCSD, La Jolla, CA 92093-0317.

Agglutinates in the size range 125-175 $\mu$ m from regolith breccia 79035 are substantially depleted in N compared with bulk 79035. Isotopically, agglutinate N closely resembles that found previously in ilmenite separates. The minimum  $\delta^{15}\text{N}$  value found during stepwise pyrolysis of agglutinates is significantly heavier than that observed for bulk 79035. The major host phase for trapped N in 79035, and the host phase of the lightest isotopic component(s), remain unidentified.

Although the cause of the long-term variation in isotopic composition of regolith N is recognised as one of the outstanding problems in lunar surface science, it is less commonly appreciated that several other aspects of lunar N isotope systematics are also poorly understood. Thus, the reason for the difference in release temperature of the two (or more) isotopically distinct components of trapped N [1] is not known with any certainty, and neither are the sources of those components, or the underlying cause of the isotopic differences between them. In addition, as first pointed out by Norris *et al.* [2], the distribution of N isotopic components among different lithic units in the regolith is not well understood. That issue is the focus of the present study.

Norris *et al.* [2] showed that agglutinates separated from soil 12023 contained trapped N that was not significantly lighter than that in the bulk sample. This was surprising because, within the context of a secular increase in  $^{15}\text{N}/^{14}\text{N}$  of regolith N [3], agglutinates, which should contain material with an earlier surface exposure, on average, than mineral grains in the same regolith sample, would be expected to contain N relatively depleted in  $^{15}\text{N}$  compared with the bulk-sample composition [4]. Put another way, since bulk 12023 was known to release  $^{15}\text{N}$ -depleted N during stepwise pyrolysis, the question becomes: What is the host phase of that isotopically light N?

We decided to revisit this problem when we found that ilmenite from regolith breccia 79035, which during stepwise pyrolysis releases some of the lightest N yet observed in lunar regolith ( $-243\text{‰}$  at high resolution [5] and  $-210\text{‰}$  at lower resolution [6]), yielded a minimum  $\delta^{15}\text{N}$  during stepwise release of only  $-180\text{‰}$  [1], as found also by Becker & Pepin [7]. A coarse pyroxene separate (175-250 $\mu$ m) yielded somewhat lighter N during stepwise pyrolysis ( $-212\text{‰}$  [1]), which is close to the minimum  $\delta^{15}\text{N}$  value observed in bulk 79035 by Clayton & Thieme [6], but the host of the  $-243\text{‰}$  component remained unidentified.

For several reasons we decided to follow up on the results of Norris *et al.* [2] by analysing agglutinates in 79035. First, the earlier study did not rule out possible release of light N from agglutinates within some restricted temperature interval. Second, although bulk 12023 yields a relatively light N component during stepwise pyrolysis, its  $\delta^{15}\text{N}$  is not particularly light ( $-32, -61$  [2];  $-15$  [8]), with the stepwise release spanning a range of about  $100\text{‰}$  [2,8]. By contrast, the minimum value for bulk 79035 is  $-243\text{‰}$  [5], with a range of about  $200\text{‰}$  [6,9]. (This latter factor may be somewhat exaggerated by the possible influence of terrestrial N at the lowest release temperatures.) Third, the constituents of 79035 were exposed on the lunar surface much earlier, on average, than those of 12023, raising the possibility of a long-term change in the style with which trapped N is distributed among lithic units in the regolith. Finally, although the agglutinate content of 79035 has apparently not been quantified, its bulk N content of about 100ppm [6,9] suggests, by comparison with other regolith samples, that it likely contains  $>50\%$  agglutinates, i.e., agglutinates probably represent the dominant lithic constituent in 79035 and must therefore be included in any study of the distribution of N within this breccia.

We therefore handpicked two agglutinate fractions from a nominally "agglutinate" (i.e., magnetic) separate (125-175 $\mu$ m) prepared by J.P. Benkert at ETH, Zurich. One consisted of irregular particles with a relatively dull surface, the other of spheroidal particles characterised by a lustrous, glassy surface. These were wrapped in Au foil, combusted in pure  $\text{O}_2$  at  $400^\circ\text{C}$  to minimise terrestrial contamination and then analysed by stepwise pyrolysis to  $1040^\circ\text{C}$ . Following pyrolysis, the first (irregular) sample was combusted at  $700^\circ\text{C}$  and repyrolysed at  $1040^\circ\text{C}$ . The second (spheroidal) sample was pyrolysed to  $850^\circ\text{C}$ , then combusted at  $700^\circ\text{C}$ , followed by pyrolysis to  $1040^\circ\text{C}$ .

Residues from these pyrolyses were kept for subsequent transfer to another system for further pyrolysis to 1700°C to extract spallogenic N.

Results are illustrated in Fig. 1. Comparison of that figure with the analogous one for 79035 ilmenite [1] shows that they are very similar, though the amounts of N released by agglutinates exceed, by a factor of about five, those released by ilmenites, presumably due to a volume-correlated component. Clearly, agglutinates in this size range are not responsible for the -243‰ component. Furthermore, the N contents of these agglutinates (20 and 26ppm), compared with whole-rock values (93ppm [6]; 114ppm[9]), are surprisingly low. For comparison, soil sample 12023 yielded 127ppmN in agglutinates and 70ppmN for the whole rock [2]. (Note, however, that our 79035 ilmenite data [1] agree closely with those from Minnesota [7] in both abundance and isotopic composition.) Either agglutinates in the size range studied here are not representative of agglutinates as a whole, or agglutinates in regolith breccias are depleted in N relative to those in soils. Size fractions of mature soil 69941, with a bulk agglutinate content probably close to that of 79035, showed only a slight lowering of  $\delta^{15}\text{N}$  with decreasing grain size [4], though a <38 $\mu\text{m}$  fraction of submature soil 79261 yielded  $\delta^{15}\text{N}$  values during stepwise pyrolysis that were systematically lighter than those for the >38 $\mu\text{m}$  fraction by some tens per mil [6].

We therefore conclude that our study of 79035 separates gives no indication that N components in agglutinates are either older than those in ilmenites or pyroxenes, or have sampled a lighter N reservoir. In fact, our data are consistent with 79035 agglutinates having incorporated N identical in abundance and isotopic composition to that trapped in ilmenites. The host phase of the lightest N component(s), and indeed the major host phase of N in 79035, remain unidentified.

[1] Kerridge J.F. et al. (1992) *Proc.Lunar Planet.Sci.Conf.22*, 215. [2] Norris S.J. et al. (1983) *Proc.Lunar Planet.Sci.Conf.14*, B200. [3] Kerridge J.F. (1980) In:*The Ancient Sun*, p.475. [4] Becker R.H. & Clayton R.N. (1975) *Proc.Lunar Sci.Conf.6*, 2131. [5] Carr. L.P. et al. (1985) *Meteoritics* 20, 622. [6] Clayton R.N. & Thiemens M.H. (1980) In:*The Ancient Sun*, p.463. [7] Becker R.H. & Pepin R.O. (1989) *Geochim.Cosmochim.Acta* 53, 1135. [8] Becker R.H. & Clayton R.N. (1978) *Proc.Lunar Planet.Sci.Conf.9*, 1619. [9] Frick U. et al. (1988) *Proc. Lunar Planet.Sci.Conf.18*, 87.

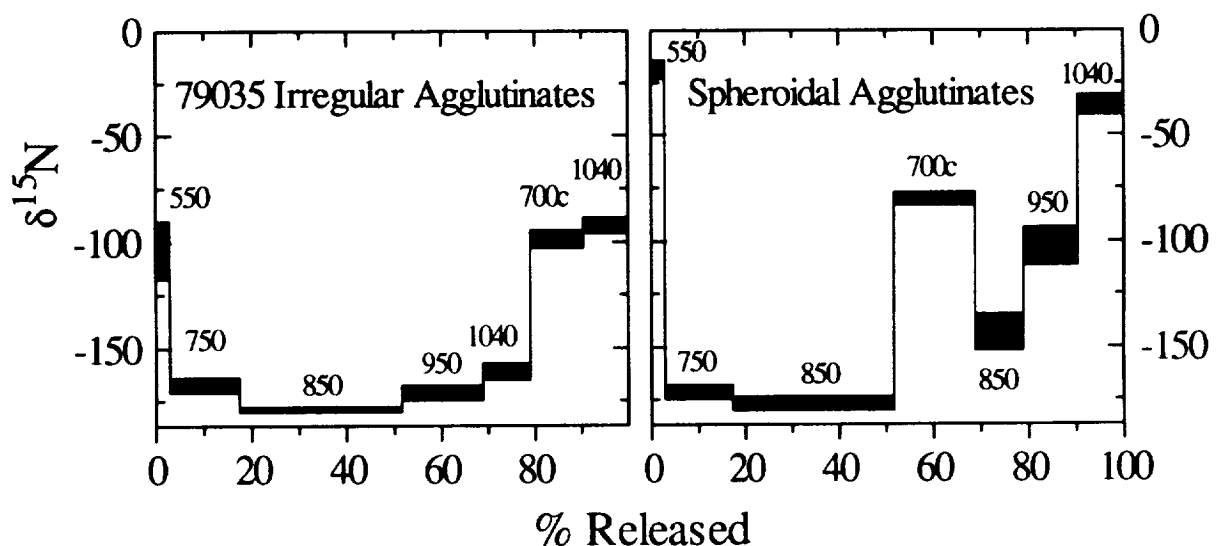


Figure 1. Isotopic composition of agglutinates separated from regolith breccia 79035, as a function of percentage of N released. Note that N released during combustion at 400°C is not included and that 1040°C was the maximum pyrolysis temperature. All steps were by pyrolysis except those marked with a "c" which employed combustion.